PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Mass Spectrometer

We, BENDIX AVIATION CORPORATION, a corporation of the State of Delaware, United States of America, of 1104, Fisher Building, Detroit, County of Wayne and State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to apparatus for and methods of distinguishing between ions of different mass. More particularly, the invention relates to apparatus for and methods of distinguishing between ions of different mass by measuring the time required for the ions to travel through a predetermined distance. The invention is especially adapted to provide a relatively sharp delineation between ions of different mass as compared to apparatus and methods now in use.

Mass spectrometers are adapted to determine masses of the different gases constituting an unknown mixture and sometimes the relative abundance of each gas in the mixture. One type of mass spectrometer makes these determinations by applying a predetermined force to a pulse of ions to accelerate the ions through a predetermined distance. The ions of relatively light mass have a greater velocity imparted to them by the predetermined force than the ions of heavy mass and, therefore, travel through the predetermined distance before the ions of heavy mass. By measuring the time required for the ions of different mass to travel through the predetermined distance the masses of the ions can be determined.

Certain operational characteristics inherent in the spectrometers now in use tend to cloud the measurements which are obtained. For example, since the ion pulse has a finite width, some of the ions of the given mass are positioned in back of the intermediate position adopted by the majority of the ions having the same mass and other ions are positioned in front of the intermediate position. Furthermore, the ions have kinetic and other energy which causes some of the ions to be travelling towards the collector plate at the instant that the predetermined force is applied and other ions to be travelling away from the collector plate at that instant. The different positioning and random motion imparted by the kinetic energy causes individual ions of a given mass to reach the collector plate at different times.

As discovered by the Applicants, it can be demonstrated mathematically that in a time-of-flight mass spectrometer having one or more regions between the ion source and the collector in each of which regions the ions are subjected to a predetermined accelerating fields, the lengths of the regions and the voltage fields prevailing across them can be so selected as to reduce to a minimum the influence of the initial positions of the ions upon the time measurement.

When using a single ion-accelerating grid as in our patent specification No. 713,993 however, the analysis leads to a practically worthless result, because the optimum arrangement is found to be such that the distance from the single ion-accelerating grid to the collector is equal to the distance from the source to said grid, regardless of the strength of the accelerating field. Such an arrangement would be obviously impracticable in that it would lead to an unacceptably short total length of the flight path.

When more than one accelerating grids are used, it is possible so to select the lengths of the regions defined thereby with regard to the voltages applied thereto, that the total length of the flight path may be extended ad libitum or practically so, whereby a time-of-flight mass spectrometer is obtained wherein the error due to the initial positioning of the individual ions is minimized or nullified, and the error due to the initial velocities of the ions may at the same time be greatly reduced, while the total flight time is still long enough to attain a high sensitivity.

This result can be achieved by using as little as two ion-accelerating grids, and our copending application No. 20291/52 (Serial No. 727,683) is directed to such an arrangement.

In some cases, however, such a two-grid arrangement, while providing the simplest way of putting to use the above-mentioned discovery, may not prove to be the best way. When the parameters of the system are such that the two fields created across the adjacent accelerating regions must differ widely from each other, a strong voltage gradient is set up in the first accelerating grid which separates the first from the second region, and interaction between the adjacent fields may objectionably disturb the flight of the particles. Moreover, the two-grid system may require an undesirably high initial voltage drop across the first region, in order to obtain a prescribed total flight distance and flight time.

By using three grids instead of two, it has been found that the above difficulties can be overcome.

In accordance with the present invention, therefore, there is provided a time-of-flight mass spectrometer having an ion-originating zone or source and an ion collector or detector with means for indicating the relative times at which the ions of different mass reach the latter, which spectrometer includes means for creating between said zone and the collector successive regions in a first one of which the ions are subjected to an initial accelerating force, in a second one of which the ions are subjected to no or substantially no accelerating force, and in a third one of which the ions are subjected to a final accelerating force greater than said initial accelerating force, the relative extents of said regions and the position of the collector or detector beyond said third region being so predetermined with respect to one another and to the values of said forces, as to minimize the error resulting from statistical uncertainty on the initial conditions at the ion source.

The invention will now be described by way of example with reference to the accompanying drawing the single figure of which is a somewhat schematic view of one embodiment of the invention, the mechanical features of the invention being shown in perspective and the electrical features being shown in block form.

In one embodiment of the invention a wedge-shaped cathode 10 made from a suitable material such as tungsten is provided. A control grid 12 is separated by a relatively short distance from the cathode and is provided with a vertical slot 14 whose mid-point is at substantially the same horizontal level as the cathode 10. The grid 12, as well as the other grids in the spectrometer, may actually be a plate with a meshed material covering the slot 14. An accelerating grid 16 is positioned relatively closely to the control grid 12 on one side and to a shield grid 18 on the other side and is substantially in alignment with both grids. Slots 20 and 22 corresponding substantially to the slot 14 are provided in the grids 16 and 18, respectively. A collector plate 24 is disposed at a relatively great distance from the shield grid 18 in substantial alignment with the grid.

A backing plate 26 is positioned slightly to the rear of the stream of electrons flowing from the cathode towards the collector plate 24 and is substantially in parallel with the direction of electron flow. The backing plate is substantially in parallel with a grid 28 positioned slightly in front of the electron flow and having a horizontal slot 30. The plate 26, the grid 28, the shield grid 18 and the collector plate 24 form a substantially closed compartment, the top and bottom of which are defined by plates 32. A horizontal slot 34 is provided in the bottom plate 32 substantially directly below the electron stream and is in communication with the flared mouth 36 of a conduit 38. The conduit in turn extends from a receptacle 40 adapted to hold molecules of different gases constituting an unknown mixture.

A grid 42 is positioned substantially in parallel with the grid 28 at a relatively short distance from the grid and is provided with a horizontal slot 44 corresponding in position and shape to the slot 30 in the grid 28. In like manner, a grid 46 having a slot 48 corresponding to the slots 30 and 44 is substantially in parallel with the grid 42 at a relatively short distance from the grid. A collector plate 50 is positioned substantially in parallel with the grid 46 at a predetermined distance from the grid, this distance being preferably relatively great. A time indicator 52 such as an oscilloscope is connected to the collector plate 50 to show the relative times at which the ions of different mass reach the plate.

The control grid 12 and accelerating grid 16 normally have positive potentials of substantially equal magnitude applied to them from a suitable power supply 54. The collector plates 24 and 50 have a slightly positive potential applied to them from the power supply 54, a positive potential being applied to the collector plate 50 to attract back to the plate any electrons produced by secondary emission when the ions impinge on the plate. The cathode 10, the shield grid 22, the backing plate 26 and the grids 28, 42 and 46 are normally at ground potential.

Because of the positive voltage on the grid 12 relative to the voltage on the cathode 10, the electrons emitted from the cathode are accelerated towards the grid. The electrons receive no further acceleration after travelling past the grid 12 since the grid 16 is at substantially the same potential as the grid 12

and the grid 18 is at ground. Therefore, any electrons that may travel through the region between the grid 20 and the collector plate 24 do not strike molecules of gas with sufficient energy to ionize the molecules.

To accelerate the ions with considerable energy towards the collector plate 50, voltage pulses of negative polarity and of approximately equal amplitude are applied to the cathode 10 and to the control grid 12 from a pulse forming circuit 56. This causes the electrons to be considerably accelerated towards the grid 16 because of the positive voltage on the grid 16 relative to the voltage on the cathode during the pulses. The added acceleration causes the electrons to travel with sufficient energy through the region between the backing plate 26 and the grid 28 to ionize molecules of gas introduced into the region from the receptacle 40.

Some of the ions produced by collision of gas molecules with electrons are retained within the electron stream since they have an opposite charge relative to that of the electrons. The ions are thus retained in a space having a relatively narrow width because of the collimating action which is provided on the electron stream by the slots 14, 20 and 22 and the collimating action which may be applied by a magnetic field (not shown). The ions are further retained in the region adjacent to the slot 30 by the repelling action produced by the positive potentials on the grid 16 and the collector plate 24. The potential well created by the electron stream and the repelling action provided on the ions by the grid 16 and the collector plate 24 cause a considerably greater number of ions to be concentrated in the region adjacent the slot 30 than is available in spectrometers now in use.

The formation of an ion pulse similar to that disclosed above is disclosed in detail in our patent specification No. 713,993.

The electron stream becomes saturated fairly quickly by the formation of ions from the gas molecules. At approximately the instant of saturation, the voltage pulses on the cathode 10 and the grid 12 are cut off to discontinue the flow of electrons towards the collector plate 24. When the electron stream is cut off, the ions are released for acceleration towards the collector plate 50. The acceleration is produced by voltage pulses applied to the backing plate 26 and the grids 28 and 42 at the instant that the electron stream is cut off or at a slightly later time. The ions of relatively light mass are given a greater acceleration by the voltage pulses than the ions of heavy mass and are, therefore, collected at the plate 50 before the ions of heavy mass. The masses of the different ions collected by the plate 50 can be determined from the relative times at which the ions reach the plate.

We have found that the measurements of ion masses obtained in mass spectrometers now in use are not as accurate as might be desired even though the ion pulses formed for use in the spectrometer are relatively strong and are relatively concentrated in space. One difficulty arises from the different positioning of individual ions in the pulse. For example, individual ions of a given mass may be positioned in back of an intermediate position occupied by a majority of the ions of that mass, and other ions of the same mass may be positioned in front of this intermediate position. This causes ions of the same mass to arrive at the collector plate at different times so that the measurements become somewhat clouded.

In addition, individual ions of a given mass and other energy before the ions are accelerated towards the collector plate. For example, individual ions of a given mass may be moving towards the collector plate before the ions are accelerated and other ions of the same mass may be moving away from the collector plate at that instant. Thus, the random motion of the ions prevents all of the ions from reaching the collector plate at the same time.

We have found that the errors in measurements resulting from the different positioning and random motion of individual ions can be minimized in spectrometers now in use by placing the collector plate at a predetermined distance from the grid before the pulse is accelerated. This distance in spectrometers employing only one grid is approximately twice the distance between the grid and the ion pulse before the pulse is accelerated. Since the distance between the ion pulse and the grid is relatively small, the distance between the grid and the collector plate is also small. This prevents the ions from travelling through a sufficient distance to become completely separated in space on the basis of their different masses and, therefore, prevents the measurements from being truly accurate.

This invention provides a mass spectrometer which compensates for any differences in the positioning and random energy of individual ions without any decrease in the distance through which the ions travel. The invention provides a first electric field of moderate intensity between the plate 26 and the grid 28, a second electric field of relatively low intensity between the grids 28 and 42 and a third field of considerable intensity between the grids 42 and 46. For example, a positive pulse of approximately 200 volts may be applied on the plate 26; positive pulses of approximately 150 volts may be simultaneously applied on the grids 28 and 42; and the grid 46 may be maintained at ground.

By providing a field of moderate intensity between the plate 26 and the grid 28, the

individual ions of a given mass which are in back of the intermediate position adopted by the majority of ions of that mass are given a somewhat greater velocity than the ions in the intermediate position. This results from the fact that the ions retarded in position are in the electric field between the plate 26 and the grid 28 for a greater period of time than the ions intermediate in position. Similarly, the ions in front of the intermediate position are given less velocity than the ions in the intermediate position.

Compensation is also provided in the electric field between the plate 26 and the grid 28 for the differences in random motion of individual ions. Thus ions of a given mass moving away from the grid 28 at the instant that the electric field is applied are given an acceleration for a longer time than ions moving towards the grid at that instant. The increased period of acceleration is obtained because the ions initially moving away from the grid must first be stopped and then accelerated in the proper direction from a standstill position.

Since the grids 28 and 42 have pulses of approximately the same amplitude applied on them, the ions travel through the region between the grids with substantially the same velocities as those imparted to them in the region between the plate 26 and grid 28. This causes the compensatory action initially imparted to the ions in the first region to be continued in the region between the grids 28 and 42. The grid 42 is disposed at the position of maximum compensation or is preferably slightly in front of this position so that a slight additional compensation can occur in the region between the grids 42 and 46. Because of the difference of 150 volts between the grids 42 and 46, a considerable acceleration is imparted to the ions in this region. This causes any errors that still remain after the compensatory actions provided in the previous region to be dwarfed. In this way, any errors that still remain are minimized. The ions then travel through the distance between the grid 46 and collector plate 50. Since this distance is relatively great, the ions become sharply separated in space in accordance with their different masses, the light ions reaching the plate 50 ahead of the heavy ions. The separation between ions of different mass is further accentuated since the ground potential on the grid 46 prevents the ions from being disturbed by the other grids during their movement towards the plate 50.

It should be realized that ion pulses may be formed in different ways than that disclosed above. Furthermore, voltages may be applied to the backing plate 26 and to the grids 28, 42 and 46 to attract the ions towards successive grids rather than to repel them from the previous grids. Different voltages than those disclosed above may also be applied on the different accelerating members as long as electric fields of predetermined intensity as disclosed above are created between the members.

There is thus provided a mass spectrometer which compensates for the different positioning and random motion of individual ions by employing a plurality of accelerating members and providing electric fields of predetermined intensity between successive pairs of members. The apparatus also provides methods of accomplishing such compensation.

What we claim is:—

1. A time of flight mass spectrometer having an ion-originating zone or source and an ion collector or detector with means for indicating the relative times at which the ions of different mass reach the latter, which spectrometer includes means for creating between said ozone and the collector successive regions in a first one of which the ions are subjected to an initial accelerating force, in a second one of which the ions are subjected to no or substantially no accelerating force, and in a third one of which the ions are subjected to a final accelerating force greater than said initial accelerating force, the relative extents of said regions and the position of the collector or detector beyond said third region being so predetermined with respect to one another and to the values of said forces, as to minimize the error resulting from statistical uncertainty on the initial conditions at the ion source.

2. A time-of-flight mass spectrometer according to claim 1, wherein the ions are subjected to substantially no acceleration between the end of the third region and the ion collector or detector.

3. An apparatus according to claim 1 or 2, which includes a backing electrode or plate on the far side of the ion source from the collector, and three spaced electrodes or grids between the ion source and the collector, and wherein means are provided for creating an electric field of a first intensity between the backing plate and the first grid nearest the source, an electric field of zero or substantially zero strength between said first grid and the second grid, and an electric field of a second intensity higher than the first between said second grid and the third grid which is nearest the collector.

4. An apparatus according to any preceding claim, wherein the ions are produced in batches or pulses, and specifically in the manner described in Claim 1 or 2 of British patent specification 713,993.

5. An apparatus according to claims 3 and 4, wherein voltage pulses of a first amplitude are applied between the backing plate and the first grid to accelerate the ions out of the ion source and through said first and second regions, and voltage pulses of a second and higher amplitude are applied between the

second and third grids to accelerate the ions through said third region and towards the collector.

6. An apparatus according to claim 5, wherein the third grid is maintained substantially at a constant, e.g. ground, potential, while positive voltages are applied in pulses to the backing plate and to the first and second grids.

7. An apparatus according to any of claims 4 to 6, wherein the voltage pulses applied to the electrodes are of sufficient duration to ensure that substantially all of the ions of any one batch are subjected to acceleration before they pass out of the corresponding region.

8. An apparatus according to any of claims 4 to 7, wherein the voltage pulses for accelerating the ions are applied at predetermined instants relative to the voltage pulses for cutting off the electron stream in the ion source as described in claim 1 or 2 of specification 713,993.

9. An apparatus according to any of claims 4 to 8, wherein the ion source generates batches of ions having a narrow initial width dimension, as measured along the path of ion travel from the source to the collector.

10. An apparatus according to any preceding claim, wherein the collector is located at a distance beyond the end of said second region considerably greater than the width dimension of any one of said first, second or third region.

11. A time-of-flight mass spectrometer substantially as described in the specification with reference to the accompanying drawing.

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731,558 COMPLETE SPECIFICATION
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.